

# Screen-printed electrochemical chromium (VI) sensing electrodes for effluent bioremediation monitoring

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## Abstract

In this work, we introduce a simple, low-cost and acid-resistant materials system for carbon-based screen-printed electrodes (SPEs), and apply it to chemical sensing of hexavalent chromium, i.e. Cr(VI), in acid environments, as encountered in bioremediation of industrial effluents. The developed composite materials comprised of 1) dense organic-carbon conductor, 2) porous polymer-carbon-ligand active sensing material, and 3) insulating and protective dielectric. All materials were formulated with two different organic matrices, polyvinylbutyral (PVB) or epoxy resin (EP). The selected ionophore for chromium detection was diethylenetriamine-pentaacetic acid (DTPA). Both variants allowed Cr(VI) sensing over a wide concentration range in acid media

**Keywords:** environmental monitoring; electrochemical sensors; bioremediation; hexavalent chromium; thick-film technology.

## Nomenclature

|         |   |      |                          |
|---------|---|------|--------------------------|
| Cetanol | 1-hexadecanol                             | PVB  | polyvinylbutyral polymer |
| DTPA    | Diethylenetriamine-pentaacetic acid       | SPE  | Screen-printed electrode |
| KS4     | Graphite powder < 4 µm, TIMCAL (CH)       | TBAC | Tributylacetyl citrate   |
| EP      | Epoxy, EpoTek 377, Epoxy Technology (USA) |      |                          |

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## 1. Introduction

Hexavalent chromium Cr(VI) is a problematic toxic and carcinogenic effluent found in waters from several industries, such as leather tannery and electrochemical plating [1,2]. Due to its environmental significance, there is a need for corresponding sensors, and thick-film screen-printed devices based on polymer-carbon electrodes, modified or not, provide a practical, low-cost alternative [3,4] to more traditional bulk electrodes such as carbon-paste [5] and glassy carbon [6].

In the case of Cr(VI) contamination of waters and effluent sludge, bioremediation strategies have been attempted using acidophilic bacteria [7]. Monitoring this process, however, requires sensors that are highly tolerant at acid pH values, e.g. ca. 1-2. Therefore, in this work, we endeavoured to study low-cost SPEs specially formulated for work in acid conditions, obtained by the incorporation of DTPA as ionophore into an acid-resistant polymer-graphite composite. This report presents the fabrication of these electrodes as well as their application to the electrochemical quantification of Cr(VI).

## 2. Fabrication of the electrodes

The electrodes were fabricated on 96% alumina substrates, by screen printing and thermal processing of thick-film inks [8]. Except the first Ag conductor layer (commercial, ESL, ElectroScience Laboratories, USA), all inks were formulated in-house (Table 1), basing on two organic matrices, EP resin (EpoTek 377, Epoxy Technology) or PVB (Sigma-Aldrich), using synthetic graphite powder KS4 (TIMCAL) as the conductive phase and DTPA as a Cr ionophore [6]. EP exhibits high chemical resistance, but has limited shelf life and even more limited pot life. Therefore, a more convenient alternative, based on thermoplastic PVB dissolved in an appropriate solvent, was also used. PVB, plasticized by TBAC (tributylacetylacrylate, Sigma-Aldrich), was chosen, as it is relatively stable in acid conditions. In contrast, in the more typical cellulose-derived screen-printing binders such as ethylcellulose, the polysaccharide glycosidic linkage is progressively hydrolysed in aqueous acid environments, leading to depolymerisation [9]. The complete materials stack (Table 1) was deposited onto elongated alumina (Al<sub>2</sub>O<sub>3</sub>) thick-film substrates (Fig. 1). Dense (to cover Ag) and porous (to allow intimate contact with the solution) carbon electrodes were formulated by appropriately changing the graphite volume fraction.

| Layer   | EP system                           | PVB system              |
|---|-------------------------------------|-------------------------|
| Ag conductor tracks & contact pads                                    | ESL 9912K                           | ESL 9912K               |
| Dense carbon layer (KS4 $\approx$ 33% vol.)                           | EP - KS4                            | PVB - TBAC - KS4        |
| Porous active carbon layer (KS4 $\approx$ 70% vol; DTPA $\approx$ 5%) | EP - KS4 - DTPA                     | PVB - TBAC - KS4 - DTPA |
| Protective dielectric   | EP - Al <sub>2</sub> O <sub>3</sub> | PVB - TBAC - cetanol    |

**Table 1. Thick-film compositions used in the fabrication of the SPEs, for EP and PVB system (see Fig. 1).**

### 3. Electrochemical characterisation

The sensors were tested using the built-in working and counter electrodes, together with an Ag/AgCl/KCl external reference electrode, using acid K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>2</sub>SO<sub>4</sub> (pH = 1) of known concentrations. The most relevant characteristic of the proposed sensors is the excellent achieved dynamic range. For instance, for the PVB-based system, this range covers Cr(VI) concentrations from 2 µM up to 25 mM. Example results achieved with this system (PVB-based materials) are shown in Figs. 2 and 3. The sensitivity and stability are very good and comparable or better than those obtained with existing electrochemical sensors. Moreover, both matrices proved to be sufficiently resistant to the harsh sensing conditions (H<sub>2</sub>SO<sub>4</sub>, pH down to ca. 1), required for the envisioned bioremediation application using acidophilic bacteria.

This combination of such an excellent analytical performance with the enormous possibilities offered by simple, low-cost disposable screen-printed electrodes opens the doors to new designs of sensors for addressing the current requirements of environmental chemical analysis.

### Acknowledgements

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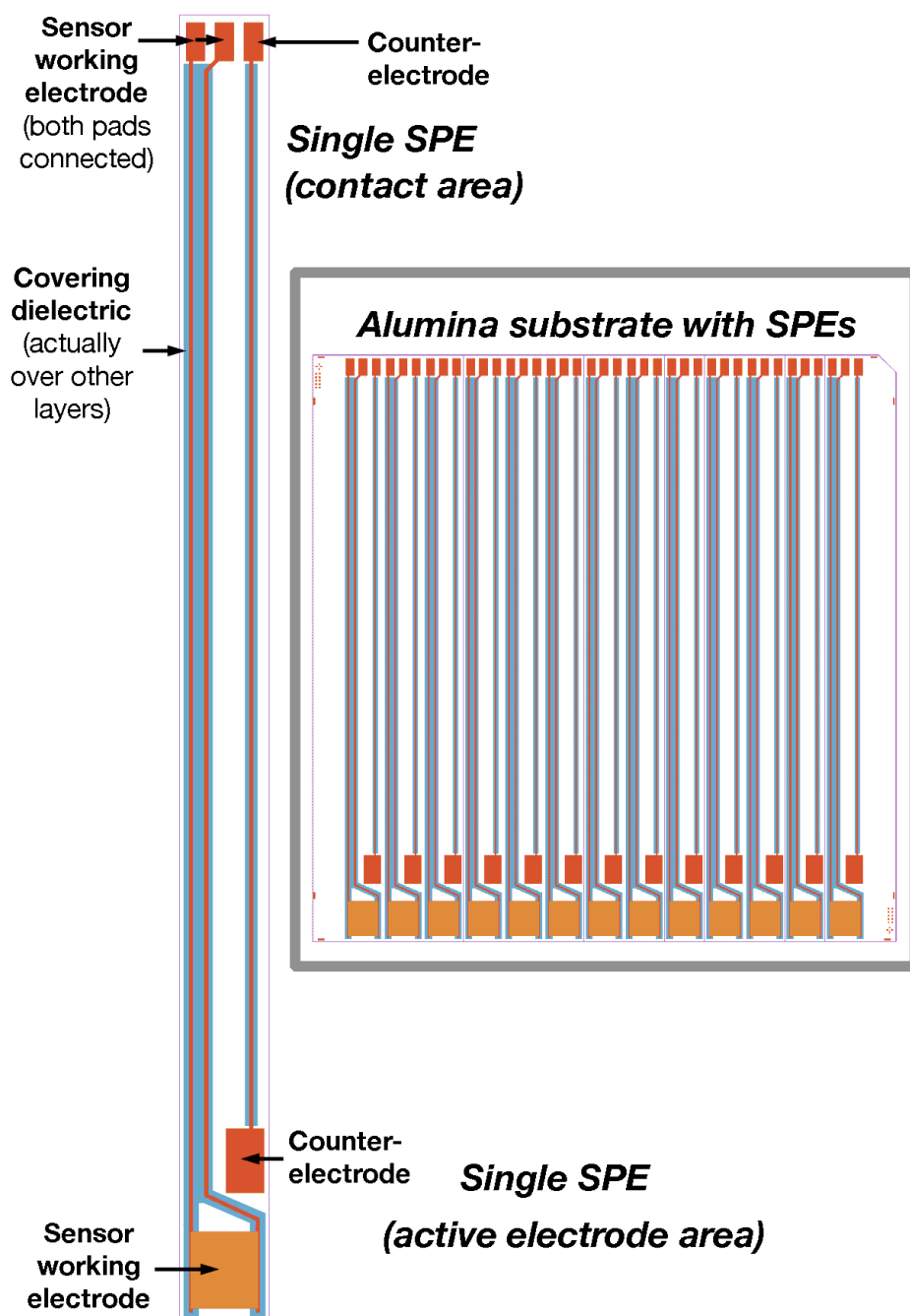


Fig. 1. Layout of SPEs, single bar and as complete substrate for batch printing on alumina (inset). Layers according to Table 1; conductors in contact with solution: dense polymer-KS4 composite (both working electrode & counter-electrode), and porous polymer-KS4-DTPA (working only).

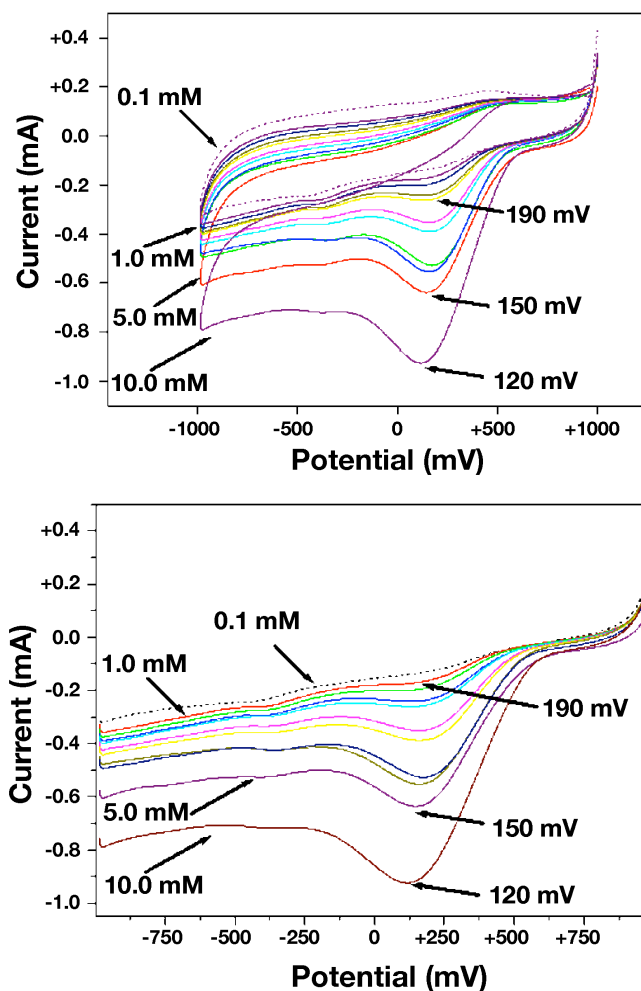


Fig. 2. Cyclic voltammograms for Cr(VI) at different concentrations, from 1.0 to 5.0 mM, with 0.5 mM intervals (the curves for 0.1 and 10 mM being also included). Top: complete scan; bottom: reduction half only. Scans performed from +1000 mV to -1000 mV to return finally to the initial potential. Scan rate: 50 mV/s. Supporting electrolyte:  $\text{H}_2\text{SO}_4$ ; pH: 1.0. Reference electrode: Ag/AgCl/KCl. Counter-electrode: graphite.

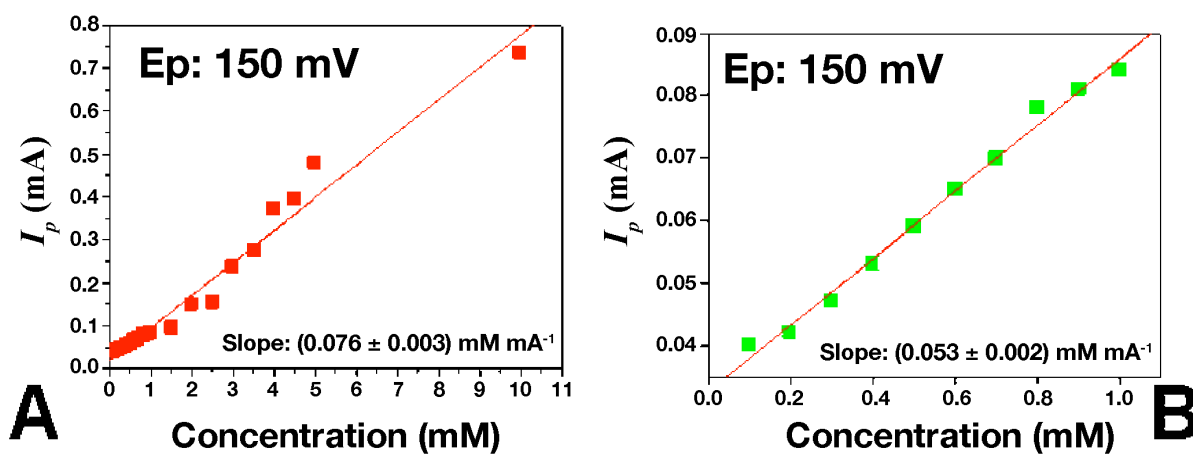


Fig. 3. Reduction peak currents at 150 mV vs. Cr(VI) concentration, as obtained from cyclic voltammograms. (A) from 0.1 to 10.0 mM; (B) inset, from 0.1 to 1.0 mM. Scans performed in same conditions as for Fig. 2.